AIR INJECTION IN CANS

A reference standard for TPO analytical methods

The quest for a TPO (Total Package Oxygen) reference standard is still open, despite the wide use of methods and devices measuring this important parameter in the brewery. Today TPO is one of the unique parameters in the beer analyst's toolbox that has no standard. In this paper, a new method to build a TPO standard is described and compared with other methods. This new standard is then used to evaluate the TPO measurement through existing methods.

Oxygen is considered a major critical parameter affecting the freshness profile of packaged beer. In 1984 K. Uhlig and C. Vilachá, working at Polar [1], published a paper that was quite a breakthrough for several reasons:

- moving from air to oxygen measurement
- moving from wet chemistry to analysis with modern instrumentation
- improvement in the low detection limit to a few ppb's, when previously it was about only 1 ml air (corresponding to 270 ppb TPO)

25 years later, another major step is reached with instrumentation manufacturers providing analysers specially dedicated to TPO. Nevertheless, today there is still a critical miss: No TPO standard reference is available. Few methods available were compared and those performances are described in this paper.
Among all methods, the air injection was identified to provide the best results. The strength of this method was demonstrated in combination with the new Orbisphere 6110 analyser.

Georges Schmidt

MSc, Mechanical Engineering of the Swiss Federal Institute of Technology of Lausanne. Product Application Manager at Hach Lange Sàrl, Geneva. In the company since 1989 (which was previously Orbisphere) where he held several positions for International Sales and Product Management

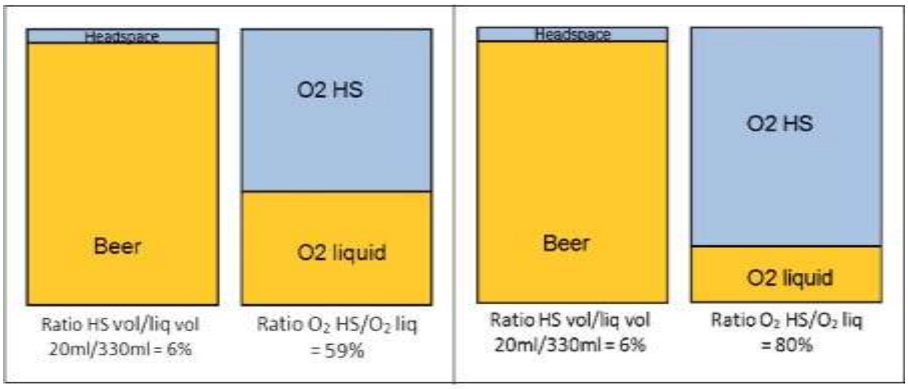


Fig. 1: Can at equilibrium, 20 ml HS vol (left)
Fig. 2: Example of a can after filling, no equilibrium (right)

What is TPO?

Figure 1 shows a 330ml can at 8°C after equilibration and figure 2 an example of a can straight after the filling. Yellow and blue areas show the beer and headspace volume with the associated O_2 content on the right. Calculation for Fig. 1 was made with the Z factor. The proportion of each surface matches the ratio of volume and oxygen content.

The TPO paradox is that the main location of the oxygen in the package is in the smallest volume: the headspace. At first, physical properties of oxygen explain this phenomenon. Being 30 times less soluble than CO2, the oxygen will remain in gas phase, with a concentration according to the temperature of the liquid and volumes ratios. This is shown in the Fig.1.

The Fig. 2 shows an average example where ratio of O_2 HS to TPO is much higher than on conditions after a perfect equilibration (Fig.1). Any HS volume variation has also an important impact on TPO, a 10ml headspace volume increase generates a TPO increase of nine per cent.

Requirements for a TPO standard

Identifying the fitness for purpose of a new TPO standard reference was evaluated by the following set of criteria [2]:

- Precision (trueness)
- Intermediate precision
- Repeatability
- Reproducibility
- Range
- Metrological robustness
- Easiness of implementation (can be deployed everywhere, lab and plant floor; less/not operator dependant)

Principles of evaluated TPO standards

The main goal for the TPO standard is to have a known amount of oxygen in a package with a known uncertainty. Many potential methods are based on the introduction of an unknown or known amount of air into the package HS. In chemical analysis this method is also called SAM (Standard Addition Method) [3].

Prior to the air injection, a batch of blanks (old beers with low oxygen) is analysed. The expected final value is the sum of the blank TPO concentration and the added air. Using the same beer than the one to measure to build the standard is also better, as it takes account of any matrix effect.

Potential solutions for TPO standards

Headspace flushed with air

Bottles are prepared in a cabinet with an oxygen controlled atmos - phere. The headspace is flushed for a defined time with oxygen controlled. This method shows good trueness and repeatability but the method requires special devices and long flushing times. This has a negative consequence on the easiness of implementation.

Water test cans

A batch of carbonated water cans is taken from a filler with known performances, in regard to the air pickup. A part of the batch is measured and the statistical TPO distribution identified. This is an easy method to implement but limitations remain when looking to provide standards with different concentrations for linearity validation purposes. Trueness cannot be identified.

This method was initially evaluated by the ASBC in 2004 and then rejected [4].

Air injection into the foam of open bottles

A bottle of pasteurised beer is carefully uncapped. The side of the bottle is gently tapped with a solid rod to induce a large amount of foam escaping the top of the bottle. A syringe of air is inserted into the foam and the contents injected. A crown is immediately replaced on top of the bottle and sealed.

This method was also evaluated by an ASBC subcommittee [4] and rejected in 2007 after an interlaboratory test. Repeatability and differences between collaborators were estimated to be not good enough.

Air injection in the HS

This is a variant of the initial ASBC method described previously. In this this method the crown cap is changed with a different one which includes a septa [5]. This method gave a repeatability and reproducibility found with a ratio std dev/ average of 28 per cent. A specific crown cap needs to be prepared specially. Trueness of 80 percent was found with the standard TPO analysis method which means a 20 per cent error.

Fig. 3: Air injection into a can

A variant of this method was mentioned by the ASBC subcommittee in the conclusion of their final report in 2007 [5]. A known amount of air is injected into an aluminum can where a rubber septa is previously stuck at the point of injection, the septa is maintained in his location with a large hose clamp.

After four years of use, this method has provided good results at Hach Lange Geneva (previously Orbisphere), either during the internal quality control tasks or field activities and requirements. The sample preparation is quite easy and this method allows the injection of almost any amount of air in the can. It therefore provides a good solution for trueness, linearity and repeat- ability criteria. Standard cans of old beer are used and the time required for the preparation and easiness of implementation are acceptable.

Methods evaluation

Table 1 shows an evaluation of all methods across different criteria. The best method should demonstrate the best combination of two main groups of criteria: metrological requirements and easiness of implementation. As several methods provide good results in either one or the other group of criteria, only the air injection method fulfils both criteria.

Air injection method applied to the Orbisphere 6110 TPO analyser

The Orbisphere 6110 measures O_2, CO_2 and HS volumes with the gases content in both the HS and the liquid. The system uses a patented gas sampling technique.

The repeatability of samples measured after the air injection with one analyser, the same operator, and at 170 ppb average, was found between ± 20 ppb down to ± 2 ppb, this last value obtained with skilled operators. The recovery ratio parameter is used as a standard validation routine. Recovery is the ratio O_2 measured/O_2 injected and ideally should be 100 per cent.

The complete measurement process is automatic and the absence of contact between sensors and the liquid minimises

Fig. 4: The Orbisphere 6110 analyser

maintenance requirements and ensures consistent operation and results reliability. Figure 5 shows the recovery distribution provided by about 70 different analysers with different analysts.

This metrological performance was obtained between different analysts, over extended timescales, with different analysers but within a single laboratory. This is sometimes known as "intermediate precision." The average recovery found was excellent, at 99.2 per cent (159 ppb) and with a standard deviation of only ± 5 per cent.

For a confidence interval of 95 per cent, measurements were found between 144 ppb and 176 ppb. Good results when considering we have an uncertainty related to both the uncertainty of the analyser and the TPO standard generation, this last being the main source of random errors generated by the operators during the standard preparation.

Linearity validation is often done during commissioning. An example is shown on Fig. 6 with a coefficient of determination R2 at 0.99 demonstrating the excellent linearity of the air injection method and the analyser.

Benefits of the new PO reference

Data from collaborative tests are not available yet but hundreds of air injections performed on different sites have shown that this method provides a higher degree of confidence with any TPO analyser or TPO method. Other benefits of the new TPO reference are:

- Identification of installed analysers uncertainty and improvement in the Quality Control management.
- The evaluation of laboratory performance by collaborative and comparison studies.
- Better outofspec production management. It will be possible to manage the product compliance by using a rejection zone, instead of a fixed single limit as it is widely used today [6].

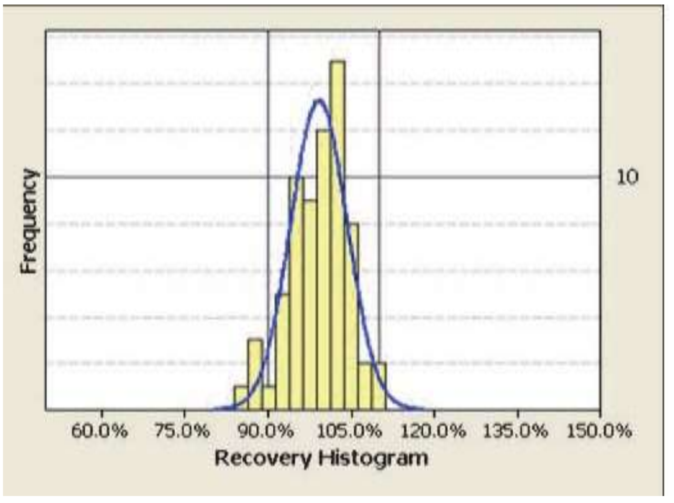
The standard TPO analysis and its limitations

Having a robust reference for TPO gives a motivation to evaluate the performance of the standard method for TPO analysis. Differences between the standard TPO analysis method and the 6110 were found in the lab and in several plants. Nevertheless, the air injection reference gave the confirmation that the 6110 was providing the correct result.

In some cases the recovery factor with the standard was found to be good, above 90 per cent, in other cases it was below 80 per cent. The standard TPO method is based on the assumption that a full equilibration of the package is reached after five minutes. This is

Table 1: Comparison of different TPO standards

Criteria	Water test cans	Air flush in HS	Air injection in foam	Air injection in HS	Air injection in cans
Precision (trueness)	◔	◑	●	●	●
Repeatability	◑	◑	●	●	●
Intermediate precision	◔	◔	●	●	●
Reproducibility	◑	◔	●	◑	●
Linearity	○	◕	●	◑	●
Range	○	◔	●	●	●
Metrogical robustness	●	◔	◔	◕	◕
Easiness of implementation	●	○	◑	◑	◕



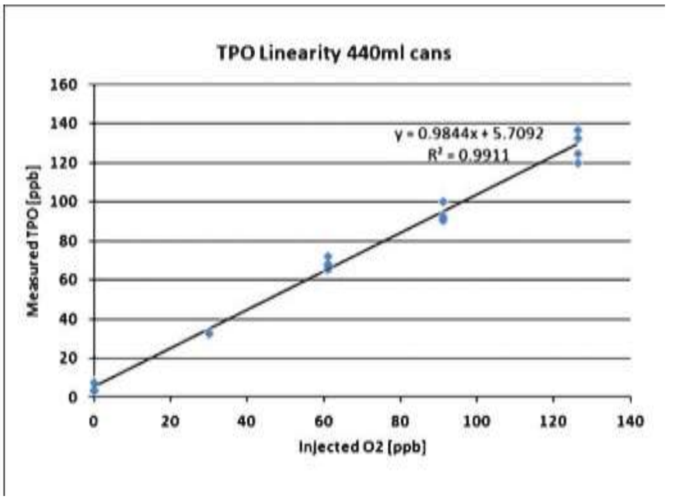


Fig. 5: Recovery histogram on Orbisphere 6110 analysers Fig. 6: Field linearity validation with air injection in cans

not always true and the gap between theory and practice is generated by main factors like:

- Bottle turners are replaced by horizontal shakers.
- The equilibration time is not the same for bottles and cans.
- Foam inside the package reduces the turbulence generation.
- Matrix effects, with or without oxygen scavengers, affecting the dissolved oxygen over the time.

Final discussion

The air injection reference in cans provides significant progress when compared with other methods. Its strength comes from its superior performances in metrological requirements and the easiness of use and implementation.

Another benefit of the air injection method is because it mimics the same air contamination process during filling operations, with the main contribution of the oxygen into the headspace. The validation of a TPO method is then done with a package having very close conditions than those found after the filling process.

The air injection method has also highlighted limitations of the stand ard TPO analysis where the measurement of the dissolved oxygen after a supposed perfect equilibration, leads to underesti - mate the TPO in many cases. The reason is the difficulty to get the correct oxygen transfer from the HS to the liquid; the equili b - rium is almost never completely reached. Because 60 to 90 per cent of the TPO is located in the HS, measuring the smallest oxygen content in the liquid exposes to a higher uncertainty when applying the Z factor.

The identification of the air injection reference performances have been made possible with the Orbisphere 6110 which does not require the need for equilibration. Finally, the use of a robust TPO standard reference will also help the transition from existing devices using the standard method to new TPO analysers. �

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